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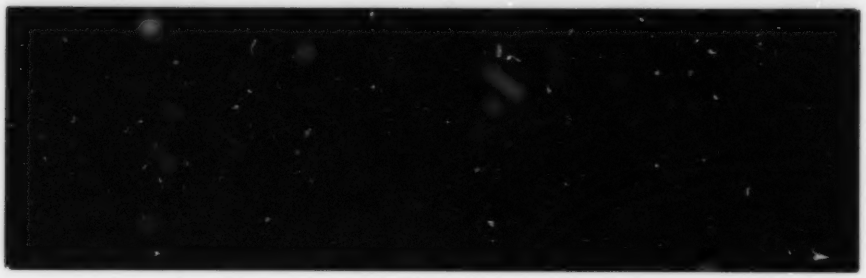

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LOCALIZED CORROSION INITIATION ON MAGNESIUM ALLOYS

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LOCALIZED CORROSION INITIATION ON MAGNESIUM ALLOYS

by

R.J. Brigham

ABSTRACT

The stability of passivity of a number of wrought and cast magnesium alloys in oxidizing basic solutions has been ranked by determining the critical chloride concentration above which pits initiate. For a wide range of alloy compositions, a narrow range of chloride concentrations caused go/no-go pitting behaviour.

LABORATOIRES DE LA TECHNOLOGIE DES MÉTAUX
RAPPORT MTL 90-51(TR)

AMORCE DE CORROSION LOCALISÉE DANS LES ALLIAGES AU MAGNÉSIUM

par

R.J. Brigham

RÉSUMÉ

La stabilité de la passivité d'un certain nombre d'alliages au magnésium forgés et moulés, dans des solutions basiques oxydantes a été établie en déterminant la concentration critique de chlorure au-dessus de laquelle s'amorcent les piqûres. Dans le cas de nombreux alliages, une mince gamme de concentrations de chlorure a occasionné un comportement "oui-non" en ce qui à trait à la formation de piqûres.

INTRODUCTION

At CANMET, the initiation of localized corrosion (pitting and crevice corrosion) has been studied extensively with alloys exhibiting passive behaviour; first with austenitic stainless steels (1,2) and more recently with martensitic stainless steel (3) and nickel (4). In all cases, it was observed that a go/no-go corrosion initiation threshold existed as a function of temperature and a theoretical approach (5) was developed to explain the stability boundary as the environment became more aggressive due to an increase in temperature or chloride concentration or a decrease in pH.

Because magnesium and magnesium alloys are known to show passive behaviour at high pH, it was decided to expand this approach to investigate the stability of the passive state in magnesium alloys as a function of temperature, chloride concentration and pH. The ranking of alloys by this go/no-go methodology addresses only the resistance to the initiation of localized corrosion and not the subsequent kinetics of attack.

APPROACH

Exploratory work in developing the approach was done on a series of wrought Mg alloys (compositions in Table 1). Coupons with dimensions approximately 38 x 38 mm were cut from the 1.5 mm thick sheets and pickled in a solution of 266 mL acetic acid and 67 g $NaNO_3$ made up to 1 L with distilled water. To minimize crevices at the contact points with the container, coupons were exposed standing on their edges in tall narrow (180 mL) beakers to which 100 mL of test solution had been added. Initial experiments were done in test solutions of pH 7, 9, 11 and 13 (by adding NaOH) with additions of 0.005, 0.05 and 0.5 M chloride as NaCl.

In solutions of initial pH 7, 9 and 11, it was observed that the pH changed to a value of approximately 10.5 in all cases within the first 24 h. In solutions with an initial pH of 13 (0.1 M NaOH), however, the pH remained approximately constant for at least 72 h whether or not localized corrosion occurred. It was further observed that the critical chloride concentration for initiation of localized corrosion (filiform and pits) was less than 0.05 M for all the alloys tested.

As a result of these observations, a series of 24 and 72 h exposures were carried out in 0.1 M NaOH solution (pH 13) containing 0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 M NaCl. After exposure, the samples were cleaned in chromic acid, weighed and examined for evidence of localized corrosion. The following trends were observed:

1. samples which appeared passive and showed no apparent corrosion suffered a measurable weight loss;
2. weight loss increased with increasing chloride concentration;
3. filiform corrosion initiated at lower chloride concentrations than pitting and tended to nucleate at the sample edge; particularly at points of contact with the beaker;

4. discrete pits on the faces of the samples (not connected with the edge) tended to appear at higher chloride concentrations and were associated with a break-away in weight loss; and
5. a reproducible go/no-go for localized corrosion as a function of chloride in 0.1 M NaOH (pH 13) was not observed either at room temperature or in an identical experiment carried out at 50°C.

At approximately this time, measurements of electrochemical potential as a function of time carried out by Mitrovic-Scepanovic (6) and reproduced in Fig. 1 show that the rest potential was not always passive, as had been assumed, but spiked from passive to active values in a periodic fashion even in 0.1 M NaOH solutions without chloride additions. It was felt that this phenomenon might be responsible for the lack of reproducibility in localized corrosion initiation results. Consequently, a series of experiments was carried out in which 5, 10 and 20 mL of H_2O_2, a strong oxidizing agent designed to maintain the potential in the noble (passive) range, were added to pH 13 solutions containing 0.005, 0.01, 0.02 and 0.03 M NaCl. In exposures of 24 and 72 hours at room temperature and 50°C, overall reproducibility improved dramatically and a standardized experimental procedure was established.

EXPERIMENTAL PROCEDURE

Based on the findings outlined above, a standardized experimental procedure was used to evaluate the resistance of wrought Mg alloys to the initiation of localized corrosion, specifically pitting, in terms of a critical go/no-go chloride concentration. This procedure consisted of the following:

1. Abrade and pickle (acetic acid plus sodium nitrate) 5 coupons with dimensions approximately 38 mm by 38 mm by the thickness of the sheet and rinse in distilled water.
2. Place the coupons in 100 mL of test solution (0.1 M NaOH containing 0.005, 0.01 or 0.02 M NaCl) to which 10 mL of H_2O_2 has been added in a tall narrow 180 mL beaker (which retains the sample in the near-vertical position).
3. Expose the coupons at room temperature for 24 h.
4. Remove corrosion products from the exposed coupons with a solution of 20% CrO_3 plus 1% $AgNO_3$.
5. Examine the coupons for pits on the flat surfaces removed from the edges and report as a percentage of the coupons showing pitting attack. For each sample, a binary (pitted/not pitted) decision is made independent of the extent (kinetics) of attack.

In the case of the cast Mg alloys supplied by the industry (compositions in Table 1), the same procedure was used after the samples were prepared. For cast plates <5 mm thick, coupons 38 mm x 38 mm x thickness were cut and tested full thickness. For cast plates of greater thickness, coupons 38 mm x 38 mm x ~2 mm were saw-cut with the original cast surface as one

side of the coupon. For slices of cast cylinders or for ingots, coupons 38 mm x 38 mm x 2 mm were cut in the most convenient orientation.

RESULTS AND DISCUSSION

Results for the wrought and cast alloys are given in Table 2 for pit initiation. An example of pitting attack is shown in Fig. 2.

Other corrosion morphologies were also observed. Magnesium without intentional alloying additions showed exfoliation in which individual grains were preferentially attacked along certain crystallographic planes. The early stages of this form of attack caused swelling at points on the surface due to apparent delamination of the magnesium crystals with interspersed corrosion products but, as attack proceeded, whole grains or parts of grains disintegrated and dropped out leaving the equivalent of large irregularly-shaped pits. An example is shown in Fig. 3. This morphology did not occur with magnesium alloys.

On magnesium alloys, filiform corrosion was commonly observed and tended to occur at lower chloride concentrations than pitting. The typical "worm track" morphology, shown in Fig. 4, tended to nucleate at the edges of coupons or at points of contact between the coupon and the container. Consequently, the initiation of filiform corrosion depended on sample preparation and exposure orientation and was not considered to be a reliable go/no-go indicator for the break-down of passivity. Once nucleated, filiform corrosion proceeded rapidly on a narrow front with the evolution of H_2 gas. The shallow corrosion track tended to grow upward (against gravity) and, in solution, appeared black in colour. When removed from solution and dried, white $Mg(OH)_2$ was the obvious corrosion product. In more oxidizing environments due to the addition of H_2O_2, the nucleation of filiform corrosion tended to be inhibited while pits tended to initiate more readily. Pits and filiform corrosion often, but not always, co-existed on the same sample.

With magnesium and magnesium alloys, increases in exposure temperature from room temperature (nominally 25°C) to 50°C had only a minor effect in promoting the initiation of localized corrosion. Although the trend was measurable, it was too small and inconsistent to use temperature as a pitting criterion. On the other hand, increasing the NaOH concentration from 0.1 M to 1 M (i.e. to pH 14) had a large effect on increasing the stability of the passive state.

The go/no-go initiation data show that the method is very sensitive to small changes in chloride concentration and is able to rank subtle changes in pitting initiation resistance. The data also show that pitting initiates in a narrow range of chloride concentrations for alloys of widely differing compositions. This observation suggests that the passive state in magnesium is not stabilized by additions of the common alloying elements. The kinetics of subsequent pit propagation has not been investigated here and may rank the alloys in an entirely different order.

CONCLUSIONS

1. Pitting and filiform corrosion initiate on passive wrought and cast magnesium alloys in basic oxidizing solutions when chloride ion is added.

2. The critical concentration of chloride which causes pit initiation has been well defined and is always greater than the value for filiform initiation.

3. The stability of the passive state of a number of magnesium alloys has been ranked in terms of the critical chloride concentration for pit initiation. Differences in stability due to a wide range of common alloying elements are small.

4. Exfoliation is observed in unalloyed magnesium above a critical chloride concentration but this morphology was not seen in magnesium alloys.

ACKNOWLEDGMENTS

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Table 1. Compositions of wrought and cast magnesium alloys (wt %)

Alloy	Al	Zn	Mn	Fe	Ni	Cu	Si	Ca	Sn	Zr	Ag	TRE	Ce	Other
Magnesium A	<0.05	<0.009	<0.10	0.007	<0.006	<0.001	<0.02	<0.001	<0.04	<0.01	–	–	<0.02	
MA	<0.05	<0.008	1.6	0.025	<0.006	<0.01	<0.02	0.065	<0.04	<0.02	–	–	0.020	
MH	<0.05	<0.008	1.6	0.018	<0.006	<0.01	<0.02	0.10	<0.04	<0.01	–	–	0.021	
FS1	3.1	1.3	0.49	0.012	<0.006	<0.01	0.020	0.10	<0.04	<0.01	–	–	0.025	
J	7.7	0.99	0.26	0.003	<0.006	<0.01	0.029	<0.001	<0.04	<0.01	–	–	<0.02	
Magnesium C	0.004	0.002	0.0015	0.0007	<0.0005	<0.0005	0.002	0.001	<0.001	–	–	–	–	
AZ31	3.1	0.88	0.47	0.0010	0.001	0.001	0.008	0.001	<0.001	–	–	–	–	
A3XA	3.4	0.003	0.003	0.004	0.001	0.001	0.005	0.001	<0.00	–	–	–	–	
Magnesium B	0.0012	<0.001	0.0036	0.0038	<0.0004	<0.001	<0.0020	<0.001	–	–	–	–	–	
AZ91D HC	9.50	0.884	0.175	0.0057	0.0012	<0.001	<0.010	–	–	–	–	–	–	
AZ91D CC	10.25	0.959	0.266	0.0043	0.0010	<0.001	<0.010	–	–	–	–	–	–	
AM60B CC	5.88	<0.010	0.266	0.0036	<0.001	<0.001	<0.010	–	–	–	–	–	–	
AZ31 (wrought)	3.01	1.04	0.439	0.0031	<0.001	<0.001	<0.010	–	–	–	–	–	–	
AZ91 D	9.0	0.69	0.26	0.0026	0.0007	0.001	0.01	–	–	–	–	–	–	
AM50 HP	5.0	0.02	0.34	0.0012	0.0005	0.001	0.01	–	–	–	–	–	–	
AM20 HP	2.0	0.01	0.48	0.0011	0.0002	0.001	0.01	–	–	–	–	–	–	
AZ91 E	8.83	0.58	0.25	0.0029	0.001	0.01	0.01	–	–	0.01	0.01	–	–	
AZ92 A	8.93	1.85	0.21	0.0022	0.002	0.01	0.04	–	–	0.01	0.01	–	–	
ZE41 A	0.01	4.53	0.01	0.0102	0.001	0.01	0.01	–	–	0.81	0.04	1.48	–	
QE22 A	0.01	0.07	0.01	0.0058	0.0046	0.01	0.01	–	–	0.72	2.29	–	–	2.03DI
ZE41	0.01	4.1	–	0.003	0.001	0.00	0.00	–	–	0.76	–	1.2	0.60	0.31La, 0.06Pr, 0.20Nd
QE22	0.01	0.0	<0.03	0.003	0.001	0.00	0.00	0.00	<0.030	0.60	–	2.2	0.03	0.00La, 0.05Pr, 2.11Nd

Table 1 (cont'd)

Alloy	Al	Zn	Mn	Fe	Ni	Cu	Si	Ca	Sn	Zr	Ag	TRE	Ce	Other
EZ33	0.01	2.2	0.07	0.002	0.000	0.00	0.00	0.00	<0.020	0.61	0.0	2.7	1.37	0.68La, 0.13Pr, 0.48Nd
WE43	–	0.014	<0.03	0.002	<0.005	<0.01	<0.01	–	–	0.56	<0.01	–	0.05	2.2Nd, 0.10Li, 4.0Y, 0.19GD, 0.28Dy, 0.13Er, 0.08Yb, 0.06Sm, factored HRE 1.0

Table 2. Pit initiation results for wrought and cast magnesium alloys

Alloy	Percentage of 5 coupons showing pitting in 0.1 M NaOH plus		
	0.005 M NaCl	0.01 M NaCl	0.02 M NaCl
Wrought			
Magnesium A	100% (ex)*		
MA	0%	100%	
MH	0%	100%	
FS1	0%	0%	100%
J	0%	0%	100%
Cast			
Magnesium B	100% (ex)		
AM60B CC	100%		
AM50HP	100%		
WE43	100%		
ZE41	100%		
ZE41A	100%		
A3XA	100%		
EZ33	80%	100%	
Magnesium C	40% (ex)	60% (ex)	100% (ex)
AZ92A	40%	100%	
AZ31	0%	40%	100%
AZ91E	0%	60%	100%
AZ91D HC	0%	80%	100%
AZ91	0%	80%	100%
AM20HP	0%	80%	100%
QE22	0%	0%	100%
QE22A	0%	0%	100%
AZ91D CC	0%	0%	100%
AZ31 (Wrought)	0%	0%	100%

* (ex) indicates exfoliation

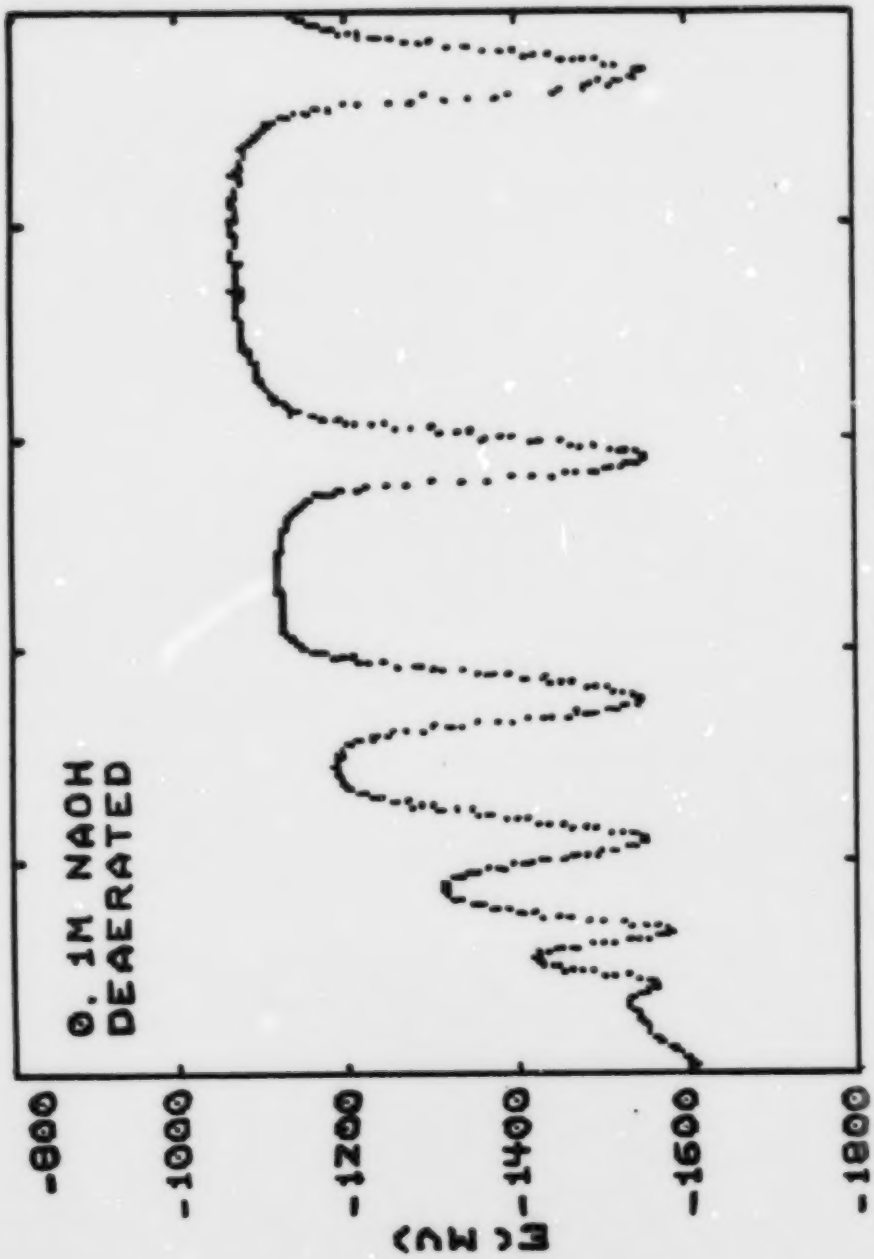

Fig. 1. Free corrosion potential of FS1 alloy as a function of time.

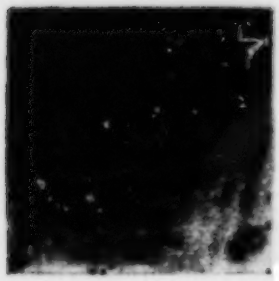

Fig. 2. Example of pitting attack of magnesium alloy. (neg 20501)

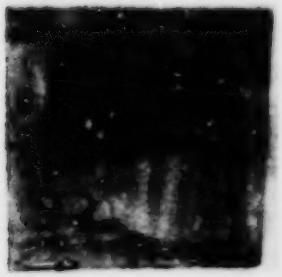

Fig. 3. Example of exfoliation attack of unalloyed magnesium. (neg 20500)

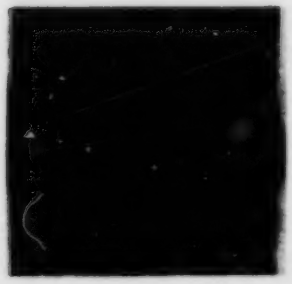

Fig. 4. Example of filiform corrosion on a magnesium alloy. (neg 20499)